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Spectrally Selective TiAlN/CrAlON/Si_3N_4 Tandem Absorber for High Temperature Solar Applications

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ABSTRACT

A new spectrally selective TiAlN/CrAlON/Si_3N_4 tandem absorber was deposited on copper substrates using a reactive direct current magnetron sputtering system. The compositions and thicknesses of the individual component layers were optimized to achieve high solar absorptance (a = 0.941-0.958) and low emittance (e = 0.05-0.07). The tandem absorber was characterized using solar spectrum reflectometer and emissometer, X-ray photoelectron spectroscopy, phase-modulated spectroscopic ellipsometry, atomic force microscopy and micro-Raman spectroscopy techniques. The experimental spectroscopic ellipsometric data have been fitted with the theoretical models to derive the dispersion of the optical constants (n and k). The n and k of the three layers indicate that the TiAlN layer is the main absorber layer, Si_3N_4 acts as an antireflection coating and CrAlON acts as a semi-absorber layer. In order to study the thermal stability of the tandem absorbers, they were subjected to heat treatment (in air and vacuum) at different durations and temperatures. The tandem absorber deposited on copper substrate exhibited high solar selectivity (a/e = 9) even after heat-treatment in air up to 550°C for 2 hrs. Studies on the accelerated aging tests indicated that the absorber coatings on copper were stable in air up to 300°C for150 hrs.

Keywords: tandem absorber; sputtering; optical properties; chromium aluminum oxynitride; titanium aluminum nitride; silicon nitride

1. INTRODUCTION

A good selective absorber is characterized by a high absorptance (α) in the wavelength range of 0.3-2.5 mm and a low emittance (ε) at higher operating temperatures [1]. The efficiency of photothermal conversion at high temperatures strongly depends on the optical properties and

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thermal stability of the component materials used in the solar absorbers. Various concepts such as absorber-reflector tandem, cermet coatings and multilayer absorbers have been used by several authors in order to achieve efficient photothermal conversion [2-6]. Among these, the absorber-reflector tandem concept has been utilized extensively to achieve high spectral selectivity [1].

In recent years, transition metal nitrides (such as TiN and TiAlN) have been used as diffusion barriers for copper metallization in micro-electronic devices and packaging applications due to their high thermal stability, chemical inertness and low electrical resistivity at higher temperatures [7,8]. TiAlN films have been used for hard coating applications because of their high hardness, low friction coefficient and excellent oxidation resistance at higher temperatures [9]. CrAlON coatings have also been developed for hard coating and phase-shifting mask applications [10]. CrAlON coatings have been reported to be stable up to 900°C in air [11]. The optical properties of TiAlN have been studied extensively which have been described elsewhere [4,5]. Whereas, the optical properties of CrAlON have not been studied so far. The TiAlN/CrAlON/Si_3N_4 tandem absorber is expected to have superior optical properties because of graded refractive indices and also because of high thermal stability of the component layers.

In this paper, we present the optical (α and ε) and structural properties of the TiAlN/CrAlON/Si_3N_4 tandem absorber prepared on copper substrates. In order to study the thermal stability, the tandem absorber was heat-treated in air and vacuum at different temperatures and durations. Solar spectrum reflectometer and emissometer, phase-modulated spectroscopic ellipsometry, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and micro-Raman spectroscopy techniques have been used to characterize the tandem absorbers.

2. EXPERIMENTAL DETAILS

TiAlN/CrAlON/Si_3N_4 tandem absorbers were deposited on copper substrates (dimensions 35 mm × 35 mm × 2 mm) using a reactive DC magnetron sputtering system that has been described elsewhere [12]. Before putting the substrates into the vacuum chamber, they were metallographically polished (rms roughness = 12.5 nm) and chemically cleaned in an ultrasonic agitator in acetone, absolute alcohol and trichloroethylene. The vacuum chamber was pumped down to a base pressure of 5.0×10^{-4} Pa. Subsequently, the substrates were cleaned in situ by argon ion bombardment for 30 min, wherein a DC bias of –850 V was applied to the substrate at an argon pressure of 6.0×10^{-1} Pa. High purity Ti-Al (99.95%), Cr-Al (99.95%) and Si (99.999%) targets were used for the deposition of the coatings. The composition of the Ti-Al and Cr-Al targets was approximately 50:50. A DC power supply was used to deposit TiAlN and CrAlON layers. Sputtering was carried out at a power density of 5 and 2.25 W/cm^2 for TiAlN and CrAlON coatings, respectively. TiAlN coating was prepared from the reactive sputtering of Ti-Al composite target in argon-nitrogen plasma at a pressure of 1.0×10^{-1} Pa and at a nitrogen flow rate of 2.5 sccm. CrAlON coating was deposited using the Cr-Al composite target in argon-nitrogen-oxygen plasma at a pressure of 1.0×10^{-1} Pa. For CrAlON deposition, the nitrogen and oxygen flow rates were 2.0 and 1.5 sccm, respectively. Si_3N_4 coating was deposited from the reactive sputtering of a silicon target in the argon-nitrogen plasma using an asymmetric bipolar-pulsed DC power supply at a pressure of 1.0×10^{-1} Pa. For the deposition of Si_3N_4, the power density was 2.0 W/cm^2 and the nitrogen flow rate was 3.5 sccm.

The optical properties of the tandem absorber were measured using solar spectrum reflectometer and emissometer (M/s. Devices and Services). The solar spectrum reflectometer measurement approximates total hemispherical reflectance and transmittance for beam radiation. The source of illumination was a tungsten-halogen lamp. The solar measurement spectrum was achieved by monitoring the reflected energy with four detectors that cover different wavelength ranges. A weighted sum of the four detectors produced a solar measurement spectrum. For the emittance measurements, the emissometer detector was heated to 82°C, so that the sample to be measured need not be heated. The reflectometer and the emissometer were calibrated with standard samples. The bonding structure of the coatings was characterized by XPS using an ESCA 3000 (V.G. Microtech) system with a monochromatic Al Ka X-ray beam (energy = 1486.5 eV and power = 150 watts). Surface imaging of the as-deposited and heat-treated samples was carried out using AFM (Surface Imaging Systems). The maximum scan ranges for AFM in the X, Y and Z-axes were 40, 40 and 4 mm, respectively.

In order to test the thermal stability, the TiAlN/CrAlON/Si_3N_4 tandem absorber deposited on copper substrates was heated in air in a resistive furnace at temperatures in the range of 300-600ºC for 2 hrs. Annealing involved increasing the temperature of the samples from room temperature to the desired temperature at a slow heating rate of 3°C/min and maintaining the desired temperature for 2 hrs. Subsequently, the samples were cooled down at a rate of 3°C/min. Thermal stability of the coatings in vacuum (5.0×10^{-4} Pa) was also studied. Accelerated aging tests have been carried out to evaluate the performance of the coatings. Changes as a result of the heating were measured using micro-Raman spectroscopy and AFM. A DILOR-JOBIN-YVON-SPEX integrated micro-Raman spectrometer was used for the present study [13].

3. RESULTS AND DISCUSSION

3.1 Absorptance and Emittance Measurements

The absorptance and the emittance values for the copper substrate, Cu/TiAlN, Cu/TiAlN/CrAlON and Cu/TiAlN/CrAlON/Si_3N_4 are presented in Table 1. A single layer of TiAlN exhibited an absorptance value of 0.772 and an emittance of 0.05. After depositing two absorber layers, TiAlN and CrAlON, the absorptance increased to 0.918. The addition of a third layer of Si_3N_4 antireflection coating further increased the absorptance value of the TiAlN/CrAlON tandem to 0.958. However, due to increase in coating thickness, there was an increase in the emittance, which resulted in a marginal decrease in the solar selectivity (a/e) from 18.3 to 16.0 [3]. The optimized TiAlN/CrAlON/Si_3N_4 tandem absorber deposited on copper substrate, thus, exhibited high absorptance in the range of 0.941-0.958 and low emittance of 0.05-0.07 at 82°C.

3.2 X-ray Photoelectron Spectroscopy

Fig. 1 shows the XPS spectra of CrAlON coating. In Fig. 1(a), the Cr 2*p* spectrum showed two peaks centered at 579.6 and 588.2 eV, which originate from Cr $2p_{3/2}$ and Cr $2p_{1/2}$ electrons in CrO_3. The doublet separation value, 8.6 eV between the two peaks also indicates that the bonding state of chromium was in the form of CrO_3 [14]. At 577.1 eV, a satellite peak of Cr $2p_{3/2}$ was observed which is attributed to the multiplet splitting caused by unpaired 3d electrons of Cr [15]. The Al 2*p* spectrum (Fig. 1(b)) showed a peak centered at a binding energy of 74.9 eV which is characteristic of AlN. In addition, a peak centered at 79.4 eV was observed which may be attributed to Cr 3s electrons of CrO_3 [14]. The O 1s spectrum (Fig. 1(c)) showed a high intensity peak centered at 530.9 eV, which represents oxygen in CrO_3. The low intensity peak at 532.6 eV originates from oxygen in Al_2O_3 [14]. The N 1s spectrum (Fig. 1(d)) showed a very weak and broad peak centered at a binding energy of 401.3 eV, which is believed to be due to impurities [16]. The bonding structures of TiAlN and Si_3N_4 layers were confirmed using XPS, the details of which have been described elsewhere [16].

Table 1 Absorptance, emittance and solar selectivity of different layers of the TiAlN/CrAlON/Si_3N_4 tandem absorber

Material	α	ε	α/ε
Cu	0.215	0.03	7.2
Cu/TiAlN	0.772	0.05	15.4
Cu/TiAlN/CrAlON	0.918	0.05	18.3
Cu/TiAlN/CrAlON/Si_3N_4	0.958	0.06	16.0

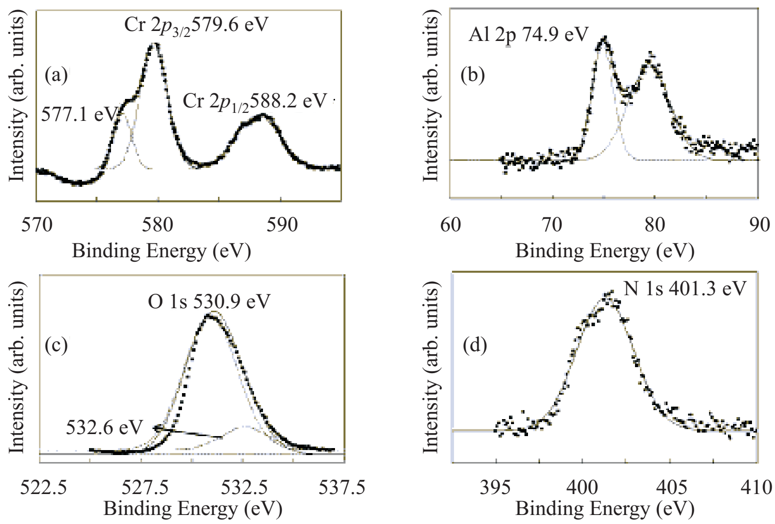

Fig. 1 Core level XPS spectra of (a) Cr 2*p*, (b) Al *2p*, (c) O 1*s* and (d) N 1*s* for the CrAlON coating.

3.3 Optical Properties

The refractive indices (*n*) and extinction coefficients (*k*) of the individual layers of the TiAlN/CrAlON/Si_3N_4 tandem absorber in the wavelength range 300-1200 nm are shown in Fig. 2. The *n* value of TiAlN layer showed a minimum at ~ 500 nm and thereafter it increased with wavelength, whereas, the *k* value increased with wavelength. The increase in *n* and *k* values with wavelength shows the metallic behavior of TiAlN. There was very little change in the '*n*' and '*k*' values of the CrAlON layer (*n* ~ 2.0 and *k* ~ 0.1) with increasing wavelength. The semitransparent behavior of the CrAlON layer is evident from its low *k* value (0.4-0.01). The '*n*' value of the Si_3N_4 layer decreased with increasing wavelength and the '*k*' value was zero throughout the wavelength range. Since the *k* value of Si_3N_4 layer was zero, the absorptance of the tandem absorber can depend only on the *k* values of the metal components in the TiAlN and CrAlON layers. These results show that the reflectance of the tandem absorber is reduced by gradually decreasing the refractive index from the substrate to the surface, consequently increasing the absorption.

3.4 Thermal Stability

Thermal stability of the solar absorber is very important since the degradation of the absorber at higher operating temperatures results in a decrease in the solar selectivity. For high temperature applications, low emittance is an important parameter, because the thermal reradiative losses of the absorber increase proportionally by T^4. Table 2 gives the absorptance and emittance values of the as-deposited and heat-treated tandem absorber.

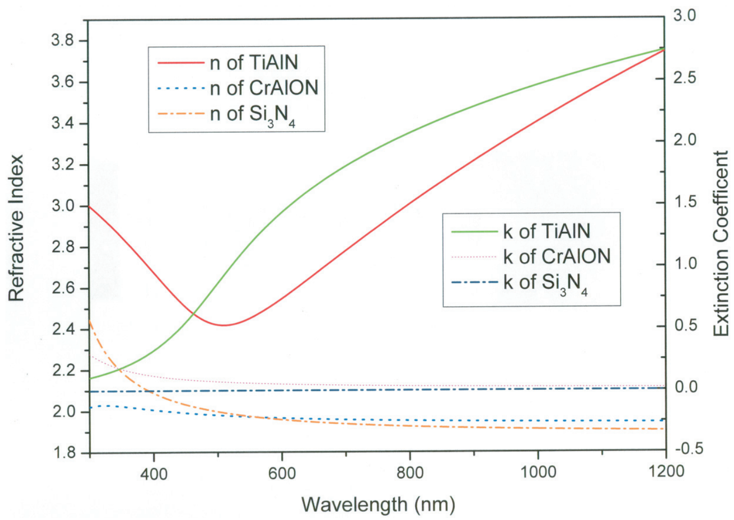

Fig. 2 Experimentally determined *n* and *k* values of the individual layers of the TiAlN/CrAlON/Si_3N_4 tandem absorber deposited on copper substrates

Heat-treatment up to a temperature of 550°C did not have a significant effect on the absorptance and emittance values of the tandem absorber. At $T_A > 550$°C, the emittance value increased drastically because of increased surface roughness and shifting of thermal re-radiation spectrum to lower wavelengths, thus overlapping with the spectrum of solar radiation [4, 17]. These results indicate that the TiAlN/CrAlON/Si_3N_4 tandem absorbers have high thermal stability in air up to 550°C and high solar selectivity of approximately 9.

Table 2 Effect of 2 hrs annealing (in air) on the absorptance and emittance values of the TiAlN/CrAlON/Si_3N_4 tandem absorber

Annealing Temperature (°C)	α As-deposited	α Annealed	$\Delta\alpha$	ε As-deposited	ε Annealed	$\Delta\varepsilon$
300	0.951	0.955	+0.004	0.07	0.06	−0.01
400	0.947	0.941	−0.006	0.07	0.10	−0.03
500	0.946	0.935	−0.009	0.06	0.08	−0.02
550	0.947	0.927	−0.020	0.07	0.10	−0.03
575	0.945	0.871	−0.074	0.07	0.13	−0.07
600	0.955	0.861	−0.094	0.07	0.15	−0.08

The three dimensional-AFM images of the as-deposited and heat-treated tandem absorber (300-600 ºC for 2 hrs) are shown in Fig. 3. The as-deposited TiAlN/CrAlON/Si_3N_4 tandem absorber showed a root mean square roughness value of 31 nm. At 600 ºC, the surface roughness of the tandem absorber increased drastically to 397 nm. The increase in the surface roughness was accompanied by an increase in the emittance of the tandem absorber. This is because emittance is a surface property and depends upon the surface condition of the material, including the surface roughness and the oxide layers [1].

The microstructural stability of the tandem absorber at higher operating temperatures was studied using micro-Raman spectroscopy. The composite Raman spectra of the as-deposited and tandem absorbers heat-treated up to 600°C are shown in Fig. 4. The spectrum of the as-deposited tandem absorber showed two broad bands centered at 238 and 605 cm^{-1}. These bands originate due to acoustic transitions in the 250-350 cm^{-1} region (LA and TA) and optic modes in the 400-650 cm^{-1} region (LO and TO) [13]. Scattering in the acoustic range is primarily determined by the vibrations of the Ti, Cr and Al ions and that in the optic range by vibrations of the N and O ions [13]. In the case of sputter deposited TiAlN and CrAlON coatings, both metal (Ti, Cr and Al) ion vacancies and light element (N and O) ion vacancies are present. The Raman spectrum did not change significantly even after heating the sample up to a temperature of 600°C, indicating a stable microstructure of the tandem absorber.

Annealing of the Cu/TiAlN/CrAlON/Si_3N_4 tandem absorber in air induces several microstructural modifications such as interdiffusion, reaction between the layers to produce a new phase, transformation within one or all layers and oxidation. These modifications result in changes in the optical properties. The high thermal stability in air (up to 550°C) of the tandem absorber in the present study is attributed to various factors. Firstly, TiAlN acts as a diffusion barrier for copper. It has been reported that the formation of TiO, AlN and Al_5Ti_2 compounds during annealing of TiAlN/Cu at higher temperatures (800-1000ºC) effectively blocks the diffusion paths for Cu, thus making them ideal diffusion barrier layers [7]. Secondly, the interdiffusion between TiAlN/CrAlON and CrAlON/Si_3N_4 is expected to be very low up to 500°C as TiAlN, CrAlON and Si_3N_4 are reported to have stable microstructures, high activation energies and very high melting points. Due to these reasons, the on-set of defect mediated diffusion and lattice diffusion is expected to be very high. Thirdly, TiAlN, CrAlON and Si_3N_4 exhibit very high oxidation resistance: 750, 900 and 1400ºC, respectively [9, 10, 18]. The tandem absorber of TiAlN/CrAlON/Si_3N_4 therefore exhibits high thermal stability and retains its optical properties even at higher operating temperatures.

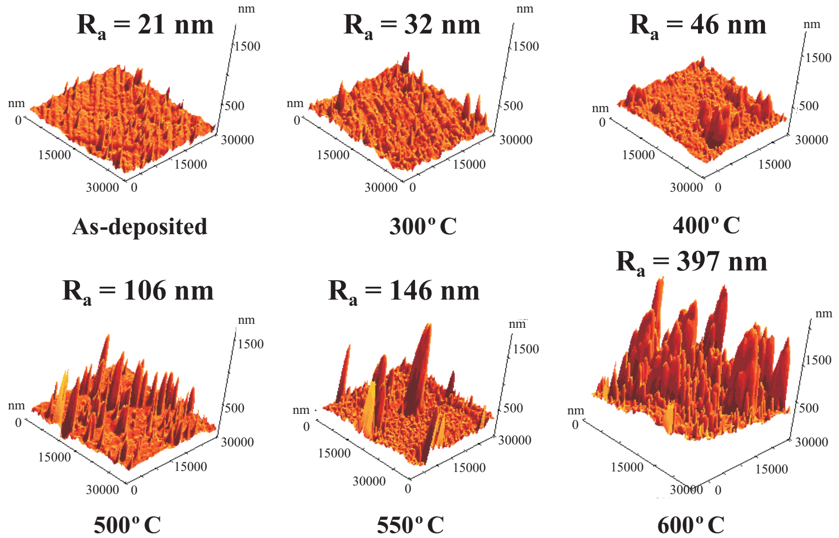

Fig. 3 Three-dimensional AFM images of as-deposited tandem absorber and tandem absorbers heat-treated at 300, 400, 500, 550 and 600°C

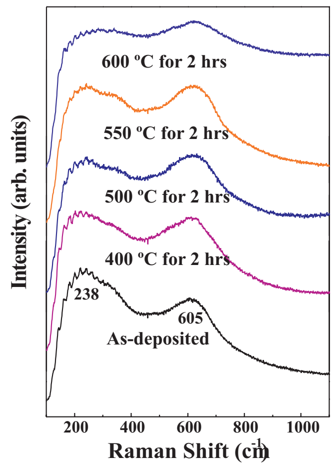

Fig. 4 Composite Raman spectra of as-deposited tandem absorber and tandem absorbers deposited on copper substrates heat-treated up to 600°C for 2 hrs in air

The tandem absorber deposited on copper substrates delaminated completely at temperatures greater than 600°C in air. Therefore, in order to test the structural stability of the tandem absorber at higher temperatures, the coatings were heated under high vacuum (5.0×10^{-4} Pa) for 2 hrs at different temperatures in the range of 700-900°C. The absorptance and the emittance values of the tandem absorber deposited on copper substrates after heat-treatment are listed in Table 3. It is clear from the table that the tandem absorber was stable up to 900°C, which was supported by the Raman data of the vacuum annealed tandem absorber (data not shown). These results demonstrate that the tandem absorber studied in the present work show no phase transformation up to 900°C as a result of heat treatment in vacuum.

Table 3 Effect of 2 hrs annealing in vacuum (5×10^{-4} Pa) on the absorptance and emittance values of the TiAlN/CrAlON/Si_3N_4 tandem absorber

Annealing		α			ε	
Temperature (°C)	*As-deposited*	*Annealed*	$\Delta\alpha$	*As-deposited*	*Annealed*	$\Delta\varepsilon$
700	0.943	0.928	−0.015	0.06	0.06	0.00
800	0.920	0.903	−0.017	0.06	0.04	−0.02
900	0.902	0.886	−0.016	0.04	0.05	+0.01

3.5 Accelerated Aging Tests

Long-term thermal stability is an important criterion for the evaluation of solar selective coatings. The TiAlN/CrAlON/Si_3N_4 tandem absorbers were heat-treated in air at 300, 350 and 400 °C for different durations. Table 4 shows the absorptance and emittance values of the heat-treated tandem absorber. The structural stability of TiAlN/CrAlON/Si_3N_4 tandem absorber was confirmed by the micro-Raman spectroscopy measurements, which are not shown here. It is clear from Table 4 that the tandem absorber was stable up to a temperature of 300ºC for 150 hrs.

Table 4 Effect of annealing (in air) on the absorptance and emittance values of TiAlN/CrAlON/Si_3N_4 tandem absorber on copper substrates for longer durations

Annealing	*Time*		α			ε	
Temperature (°C)	*(hrs)*	*As-deposited*	*Annealed*	$\Delta\alpha$	*As-deposited*	*Annealed*	$\Delta\varepsilon$
300	150	0.941	0.908	−0.033	0.06	0.06	0.00
350	100	0.930	0.830	−0.100	0.05	0.05	0.00
450	50	0.926	0.816	−0.110	0.06	0.12	+0.06

4. CONCLUSIONS

The optimized TiAlN/CrAlON/Si_3N_4 tandem absorber deposited on copper substrates exhibited high solar absorptance in the range of 0.941-0.958 and low emittance of 0.05-0.07 at 82°C. Ellipsometry results indicated the graded refractive index nature of the TiAlN/CrAlON/Si_3N_4 tandem absorber. Heat treatment of the tandem absorber in air for 2 hrs at 550°C did not affect the absorptance (0.927) and emittance (0.10) significantly. These tandem absorbers were also found to be stable in air for longer durations (300°C for 150 hrs). The Raman data confirmed the microstructural stability of the coatings in air (550°C) and vacuum (900°C).

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